Release of Contaminant U(VI) from Soils

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Abstract: The retention, mobility, and bio-availability of U(VI) in contaminated soils depend strongly on release of U(VI). Laboratory batch experiments were performed to evaluate the factors controlling the release of U(VI) from contaminated soil at Oak Ridge, Tennessee. We found that the ionic strength of the extraction solution strongly affects release of U(VI). Increase in ionic strength shows a strong effect on U(VI) release as indicated by the increase in release rates and associated release of U(VI) concentrations. We also found that the ratio of solution volume to solid mass (V/M) has a significant impact on the release of U(VI). Increase in the V/M ratio shows a negligible effect on the U(VI) release over a 4-day period. However, at Day 30 and Day 120, larger V/M ratios cause greater U(VI) release. The maximum U(VI) concentrations observed in the release experiments are in the range of schoepite estimated under conditions relevant to the experiments, suggesting that schoepite solubility primarily controls the U(VI) release, but that solubilization and desorption effects cannot be distinguished using macroscopic methods.

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Introduction

Uranium (U) contamination of the subsurface resulting from past radioactive waste disposal and storage practices represents a serious environmental contamination problem at a number of United States Department of Energy (DOE) sites. Remediation work is urgently needed to lessen the environmental impact of mobile uranium and radionuclides. The Field Research Center (FRC), located on the Oak Ridge Reservation in eastern Tennessee, is one of the DOE Natural and Accelerated Bioremediation Research (NABIR) Program's major research sites (*1*). Three areas in the U contaminated zone around the former S-3 ponds have been designated as the primary targets for NABIR field studies (*1*). In addition, one background area was established at the FRC for comparison studies in an uncontaminated environment. Many studies are being conducted at the FRC and in laboratories using FRC sediments to identify processes that can stabilize uranium and other radionuclides (*2*). Because soils contain a variety of solid phases capable of retaining U(VI), understanding the factors controlling the release of U(VI) from contaminated soils is essential (*3-5*).

Efforts are being made to decontaminate U-affected soils, commonly through biogeochemical immobilization and chemical removal. The removal of U(VI) from contaminated soils through chemical leaching is based on the formation of soluble complexes. In general, this approach can remove a much higher percentage of U(VI) than is bio-available (*5*). Two DOE sites, the Fernald Environmental Management Project site near Fernald, Ohio, and the Savannah River site, South Carolina, have used this approach for *ex situ* removal of U(VI) (*6-8*). The release of U(VI) by chemicals, however, remains a challenge, because it is constrained by a variety of factors, such as complexing anions, solution pH, dissolution kinetics, and aging (e.g., *3, 9, 10*). The mechanisms responsible for the U(VI) release are not yet fully understood. To select optimal parameters for U(VI) solubilization and to better understand the factors governing U(VI) stabilization, U(VI) release studies are needed that include analyses of release kinetics and controlling factors .

U(VI) in contaminated soil occurs in different chemical forms ---water soluble, exchangeable, carbonate-associated, iron/manganese-oxide- associated, organic-matter-bound, and mineral structured (e.g., *6, 11*). Except for mineral structuredU(VI), U(VI) can be readily removed by chemicals that do not dissolve major soil minerals (*3, 5, 6*). U(VI) associations may occur through various mechanisms, including (1) bio-sorption (organic matter-bound forms) (*12, 13*); (2) sorption onto Fe-oxide minerals (*14-17*); (3) occlusion of U(VI) by Fe-oxide mineral and clay coatings (*13, 18*); (4) co-precipitation of U(VI) with naturally occurring mineral phases such as oxides, carbonates, and silicates (e.g., *19, 20*); (5) colloid coagulation and aggregate precipitation (*21, 22*). Therefore, identification and quantification of contaminant U(VI) associations provide information relevant to release of U(VI) from contaminated soils.

The purpose of this study is to measure release ofU(VI) from a contaminated Oak Ridge soil in batch reactors to determine the factors controlling release of U(VI), including ionic strength of extraction solution and solution volume to solid mass ratio (V/M). The U(VI) concentrations released under these conditions are then compared to U(VI) solubilities.

Materials and Methods

Chemicals. All chemicals used were analytical grade and used as received. The solutions were prepared with distilled water.

Soils. Soil used for U(VI) release experiments were acquired from the FRC Area 2 (denoted OR2), which has a history of radionuclide waste disposal and subsurface contamination (*1*). The soil was homogenized inside a nitrogen-filling glove bag. Following some initial characterization work, subsamples from the homogenized soil

were taken for the release experiments reported here (Additional information on soil properties not cited here can be found in (*23*)). In addition, two uncontaminated soils, one from the FRC background site (denoted ORB) and another soil from Altamont Pass in California (denoted AP) were selected to assess the effect of contaminant aging on U(VI) chemical forms. All soil samples were disaggregated and passed though a 2 mm sieve to remove gravel. The sieved soils were then air-dried. The dried OR2 soil was analyzed by synchrotron X-ray adsorption spectroscopy (XAS) at the GSECARS Beamline 13-IDC, Advanced Photon Source, Argonne National Laboratory, which revealed that 95%±5% of the uranium was in the hexavalent oxidation state (data not shown). The ORB and AP soils were contaminated with 1.2 mg L^{-1} of U(VI) solution (UO$_3$) at pH 7 following a U(VI) sorption procedure described previously (*24*), and then aged in vials for 180 days. The three soils used have relatively high silt and clay fractions as shown in Table 1.

U(VI) chemical forms in the soils were operationally identified and quantified by using the sequential extraction approach proposed by Miller et al. (*25*) and used by others for U fractionation (*6, 11, 26*). The extraction solutions and the U(VI) chemical form determined here in order : distilled water ---water soluble; 0.5 mol L^{-1} Ca(NO$_3$)$_2$ ---exchangeable; 0.44 mol L^{-1} C$_2$H$_4$O$_2$ + 0.5 mol L^{-1} Ca(NO$_3$)$_2$ ---carbonate; 0.1 mol L^{-1} Na$_4$P$_2$O$_7$ ---organically bound; 0.18 mol L^{-1} (NH$_4$)$_2$C$_2$O$_4$ + 0.1 mol L^{-1} H$_2$C$_2$O$_4$ ---amorphous oxides; and concentrated H$_2$SO$_4$+HNO$_3$ ---mineral form. The extractions were performed in sealed 50 ml vials. A V/M ratio of 40:1 was used, except for the mineral associated---form, which was determined by applying concentrated HNO$_3$ and H$_2$SO$_4$ acid at a V/M ratio of 15:1. This procedure for estimating the mineral associated form was also used for determining the total U(VI) in the soils. All conditions were tested in

triplicate. Initially, water soluble U(VI) was measured over a three-day equilibration period. Subsequent steps followed the procedures addressed above. A selected solution was added to the soils used in the preceding step. Each extract solution was recovered by centrifugation at 4000 rpm for 47 min (0.1μm cutoff) and then analyzed for U(VI). The soils were washed two times with 0.01 mol L^{-1} $CaCl_2$ between each extraction step.

Release Experiments. Two studies were conducted to evaluate the release of U(VI) from the OR2 soil in batch reactors at a relatively constant pH of about 7.5. The first study examined ionic-strength effects on U(VI) release, whereas the second examined the effect of solution-volume-to-solid-mass ratio (V/M) on U(VI) release. Both ionic-strength and V/M-ratio factors were considered, because previous investigations indicated that they significantly affect U(VI) partition in subsurface environments (*27-29*).

Ionic strength effect on U(VI) release: The ionic strength of the solutions was adjusted by adding $NaNO_3$ because Na^+ and NO_3^- are likely to be the dominant cation and anion, respectively, in groundwater at the contaminated FRC site. However, it should be noted that NO_3^- does form aqueous complexes with U(VI). Although such complexation is relatively weak in the neutral pH range, the high concentrations of NO_3^- in the solution may enhance solution ionic strength and likely influence U(VI) removal. The range of ionic strength considered was from 0.01 to 1.0 mol L^{-1}, roughly covering the ionic strength range observed in the FRC groundwater (*1*). A V/M ratio of 10:1 was applied. All samples were prepared in triplicate, except samples at Day 30 (duplicate). Suspensions were vigorously agitated in a shaker for 24 hours and then kept hydrostatic until sampling times. The initial pH of the different-ionic-strength $NaNO_3$ solutions was

around 5.6; however, the pH soon increased to about 7.5 when the solutions were well mixed with the OR2 soil, because of calcite dissolution. The dissolution of calcite keeps soil pH circum-neutral where U(VI) has limited solubility (e.g., *25, 30*). Solutions were analyzed after 4, 30, and 120 days. Samples were shaken overnight just before centrifuging and then   centrifuged at 4000 rpm for 47 minutes. After 5 ml of supernatant was collected from each vial, its pH was measured and its U(VI) concentration was determined (as described later).

V/M ratio effect on U(VI) release: The extraction solution used was $NaNO_3$ with an ionic strength of 0.01 mol L^{-1} and an initial pH of 5.6. The V/M ratio range considered was from 2:1 to 100:1. The broad V/M ratio range chosen aims at comparing the results from the release and previous sorption experiments (*24*)under nearly identical conditions. The solution pH immediately increased to about 7.5 when the extraction solution was completely mixed with OR2 soil, independent of the V/M ratio used. Procedures similar to those described in the method for examining the ionic-strength effect on U(VI) release were followed.

To evaluate the time-dependence of U(VI) release, experiments were conducted for 120 days. pH was maintained at 7.5 ± 0.2, and no pH adjustments were made during the entire experiment.

The U(VI) concentrations released (C) with time (t) can be appropriately described using the following equation with two fitting parameters a and b:

$$C = \frac{at}{(b + t)}$$

(1)

The U(VI) release rate, R, in mol g^{-1} s^{-1}, can then be estimated from the time derivative of equation 1.

$$R = \frac{\partial C}{\partial t} = \frac{ab}{(t^2 + 2bt + b^2)} \qquad (2)$$

Geochemical Calculations. U(VI) solubility as a function of both ionic strength and V/M ratio were estimated using PHREEQC 2.0 with the Wateq4f database (*31*). Based on the calcite concentrations in soils shown in Table 1, the total calcite contents were estimated for U(VI) solubility calculations with respect to V/M ratio and ionic strength conditions. U(VI) speciation was calculated in a pH range of 7.3 to 7.7 under conditions relevant to the experiment.

Analysis. U concentrations were determined using a Kinetic Phosphorescence Analyzer (Model KPA-11, Chemchek Instruments, Richard, WA, USA). The KPA has a detection limit of 0.1 ppb. To determine interferences from the extraction chemicals on U(VI) measurement via KPA-11, samples were spiked with U(VI) standard. U(VI) recovery was in the range of 95–105%.

Results and Discussion

Ionic-strength effects on U(VI) release. The release of U(VI) as a function of ionic strength is shown in Figure 1a. The ionic strength used within the range of 0.01 to 1.0 mol L^{-1} has a positive influence on the U(VI) release. The mass balance among different U(VI) phases is as follows:

$$U_{total} = U_{sorbed} + U_{aqueous} \qquad (3)$$

$$U_{total} = S_U \times M + A_U \times V \qquad (4)$$

where S_U and A_U are the remaining U(VI) concentrations in the solid phases ($\mu g\ g^{-1}$) (ignoring the "mineral associated" fraction), and aqueous concentration ($\mu g\ L^{-1}$),

respectively. If the release coefficient, R_d is defined here as the ratio of U(VI) retained in solid phases to U(VI) released in aqueous phase (mL g^{-1}), the following equation holds:

$$\frac{U(VI)_{total}}{M} = (R_d \times A_U) + (A_U \times \frac{V}{M})$$ (5)

Hence,

$$R_d = \frac{U_{total}}{M \leftrightarrow A_U} - \frac{V}{M}$$ (6)

where V is the solution volume (mL) and M is the solid mass (g).

To quantify the total extractable U(VI) in the soils used, we applied a sequential extraction approach as described previously. In the present study, six operationally defined forms were considered: water soluble, exchangeable, carbonate-associated, organic carbon-bound, amorphous phase-associated and mineral structural U(VI). Figure 2a shows U(VI) concentrations in different U(VI) forms, along with the percent distribution of U(VI) in each phase for the OR2 soil (Figure 2b). About 50% of the U(VI) in this soil is associated with mineral structure. Approximately 40% of U(VI) occurs in the sum of carbonate and organic carbon phases. The percentage of U(VI) in the amorphous phases is about 5%, and the total percentage of water soluble and exchangeable U(VI) is around 5%.

Similar results were obtained for the aged ORB and AP soils contaminated with U(VI) (Figure 2a and 2b). In recognizing that selectivity and redistribution were likely incomplete during the sequential extraction (31,32), the percentages of different U(VI) fractions shown in Figure 2b could vary. Because clay minerals, alumino-silicates, and crystalline iron oxides are dominant in the OR2 soil and are poorly soluble with the extraction chemicals used, leaching with these reagents is unlikely to remove U(VI)

9

bound within mineral structures (*4,11*). The concentration of U(VI) in the strong-acid-extracted fraction gives an estimate of insoluble U(VI) residing in the soil. Thus, an average value of 102 µg g^{-1} was assumed to represent the total extractable U(VI) in the OR2 soil. The resulting R_d values, computed from Equation 6 with respect to ionic strength, are shown in Figure 1b. An increase in ionic strength yields a decrease in R_d (i.e. an increase in U(VI) in solution).

U(VI) releases increased from Day 4 to Day 30, and continued increasing (to a lesser extent) up to Day 120. From the R_d results shown in Figure 1b, we see large differences of R_d between Day 4 and Day 30 , and R_d at Day 30 is in fair agreement with R_d at Day 120 with respect to different ionic strengths.

With the R_d values and U(VI) concentrations released, the remaining U(VI) in the OR2 soil can be readily calculated. Normalized to the total extractable U(VI), removal ratios of U(VI) from the OR2 soil with respect to ionic strength are shown in Figure 3. The maximum removal of U(VI) from the OR2 soil reaches approximately 24% at the highest ionic strength , which is still significantly lower than the 50% of U(VI) removed by using either 0.2 mol L^{-1} NaHCO$_3$ (pH $\approx$ 10) or 1.0 mol L^{-1} HNO$_3$ (pH $\approx$ 0) in 30 days (data not shown).

The release rates of U(VI) with respect to ionic strength at different time periods are presented in Figure 4. At Day 4, the release rates were in the range of 10^{-14} mol g^{-1} s^{-1}, approximately 10 and 100 times larger than those rates at Day 30 and Day 120, respectively. Within a given period, release rates of U(VI) generally increased with higher ionic strength. Similar results for the release rates of U(VI) were obtained when the U(VI) concentrations released (C) are fit using a third-order-polynomial, i.e., $C = a\,t^3$

+ b t^2+c t (in which a, b, and c are the fitting parameters) Then, the time-derivative of the mentioned equation is taken.

To better understand U(VI) release, U(VI) solubility as a function of ionic strength within a pH range from 7.3 to 7.7 was calculated with respect to schoepite (P_{CO2}=$10^{-3.5}$ bar), as shown in Figure 5. Schoepite was selected because its solubility is the smallest among U(VI)-bearing minerals depleted in Si and PO_4^{3-} in the neutral pH range (*25*). Within the lower pH range from 7.3 to 7.5, schoepite solubility ranges from 1.0 to 1.5 mg L^{-1}, slightly dependent on ionic strength. In contrast, within the slightly higher pH range from 7.5 to 7.7, schoepite solubility ranges from 1.5 to 5.0 mg L^{-1}, shows a larger variation, and is more strongly dependent on ionic strength. Schoepite solubility at pH 7.5 as a function of ionic strength (solid line in Figure 1a) is in the same range as U(VI) concentrations at Day 30 and Day 120 in the release experiments, suggesting schoepite solubility as a possible controlling factor in the measured U(VI) released. In addition, removal ratios of U(VI) estimated from schoepite solubility at pH 7.5 (solid line in Figure 3) coincide with the removal ratios at Day 30 and Day 120, again suggesting that schoepite solubility may influence the degree of U(VI) release from these soils.

In the neutral pH range, the uranyl ion (UO_2^{2+}) readily forms a variety of aqueous carbonate complexes and surface complexes (*7-9*). Speciation calculations in a pH range from 7.3 to 7.7 show that uranyl carbonate complexes, particularly calcium uranyl carbonate complexes (e.g., $Ca_2UO_2(CO_3)_3$) (*33-36*), account for more than 99% of the soluble U(VI). The activity of such complexes shows strong ionic strength dependence (data not shown). An increase in solution ionic strength promotes U(VI) desorption (*27*).

The good correlation between U(VI) released and ionic strength supports the presence of sorbed U(VI) in the OR2 soil.

Similar results are also obtained by Mason et al. (*7*) when bicarbonate was used for adjusting ionic strength. Recently, Elias et al. (*37*) observed an increase of U(VI) extracted with increasing concentrations of $NaHCO_3$ and indicated that 1.0 mol L^{-1} $NaHCO_3$ at pH 8.3 is the most effective regent for removal of surface complexed U(VI). Gadelle et al. (*38*) also reported that the release efficiency of U(VI) increases with an increase in $NaHCO_3$ concentration. In addition to complexing U(VI), carbonate concentration may influence the formation of colloids, further influencing U(VI) release. Wang et al. (*21*) reported U(VI) release from boom clay in carbonate media and found that U(VI) in solution is present in colloidal form at bicarbonate concentrations lower than 0.1 mol L^{-1}. At higher bicarbonate concentration, U(VI) was only present in soluble form. The soluble concentration of U(VI) increases significantly when $NaHCO_3$ concentration is above 0.3 mol L^{-1}, suggesting that U(VI) carbonate complexes enhance U(VI) release from soils.

V/M ratio effects on U (VI) release. The V/M ratio significantly influences U(VI) release (Figure 6a and 6b). R_d values as a function of V/M ratio were calculated on the basis of Equation 6; data are presented in Figure 6b. R_d values increase appreciably from V/M ratio 2:1 to 40:1, and increases slightly after 40:1. Over time, there is an increase in U(VI) concentration, but only small changes were observed after 30 days for the small V/M ratios (2:1 to 10:1), while the high V/M ratios (40:1 to 100:1) still exhibited moderate increases.

Following the same procedure as before, the remaining U(VI) in the OR2 soil was calculated with respect to R_d and U(VI) concentrations released. Normalized to the total extractable U(VI), the removal ratios of U(VI) in the OR2 soil as a function of V/M ratio with time are presented in Figure 7. More U(VI) was released with an increased V/M ratio, with about 24% of the total extractable U(VI) released in the largest V/M ratio (100:1) batches at Day 120. The U(VI) removal ratios are very limited and relatively independent of V/M for the Day 4 batches. This relatively consistent short-term U(VI) release likely represents the original soluble and sorbed U(VI) phases in the OR2 soil. The sequential extraction results show that U(VI) concentrations in both water- soluble and exchangeable forms are approximately 12% of the total extractable U(VI), appreciably larger than the U(VI) removal ratio at Day 4.

The release rates of U(VI) with respect to V/M ratio at different time periods are presented in Figure 8. At Day 4, the release rates are in a range of 10^{-15} mol g^{-1} s^{-1}, nearly 10 times lower than Day 4 rates in the ionic-strength tests and much larger than those rates at Day 30 and Day 120. Release rates increased with increased V/M ratio, except the V/M ratio batches at Day 4.

With the solution used and the V/M ratio considered, U(VI) solubility was calculated with respect to schoepite within a pH range of 7.3 to 7.7; results are presented in Figure 9. Within this pH range, schoepite solubility strongly depends on V/M ratio, because dissolved carbonate concentrations are different with respect to different V/M ratios. In a pH range from 7.3 to 7.7 , equilibrium calcite dissolution ranges from 9.74×10^{-3} mol L^{-1} to 1.37×10^{-1} mol L^{-1}. Thus, V/M ratio-dependent batches (except 2:1 batches) at this pH range can dissolve all calcite present in the soil used. Schoepite solubility at pH 7.5 with

respect to V/M ratio (solid line in Figure 6a) is in approximate agreement with the results of the smaller V/M ratio batches (2:1 and 10:1) shown in Figure 1a at Day 30 and Day 120, suggesting solubility as a controlling factor in the U(VI) released. Large differences between schoepite solubility and released U(VI) concentrations were observed for the larger V/M ratios (>10:1). Removal ratios of U(VI) estimated from schoepite solubility at pH 7.5 (solid line in Figure 7) agree with the removal ratios of the smaller V/M ratio batches. The lower amounts of U(VI) released with the larger V/M ratios suggest that U(VI) release will continue, assuming that schoepite dissolution is a controlling factor.

The V/M ratio has long been recognized as a key parameter influencing radionuclide partitioning between solution and solid phases (*39*). Increasing reagent volume to directly enhance U(VI) removal has been reported (*3*). Elias et al. (*37*) found that between 1:1 to 8:1 V/M ratios, U(VI) steadily increased , but observed no change with further increase in V/M ratio. Differences with our results may stem from the experimental procedure and period, the possible presence of different U(VI) forms in soil, and the reagents used. V/M-dependent U(VI) removal is a process resulting from the interaction of a number of different processes such as ion-exchange, dissolution, complexation, and desorption (*6-9*). In our experiments, slow mass transfer between the soil and water also probably delayed equilibration.

R_d values are often interpreted to be independent of the solid-to-liquid ratio used in previous batch experiments (*40, 41*). Our data show that R_d is dependent on the V/M ratio because U(VI) dissolution and precipitation are strongly V/M dependent in calcareous soils.

Comparison of K_d and R_d

Both the distribution coefficient, K_d, and release coefficient, R_d, are described by a ratio of solid-associate concentration to aqueous concentration, but the former is often assumed to represent an equilibrium process(*42*). Figure 10 shows R_d values estimated from Equation 6 and the total extractable U(VI) for V/M dependent batches at Day 4, and K_d from previous sorption experiments (*24*) as a function of U(VI) concentration. The soil used in the sorption study is from the same site and has similar composition (Table 1). Under the same U(VI) concentration and time, the K_d and R_d values are fairly similar, in spite of the differences in V/M ratios. The differences in K_d and R_d are probably also a result of kinetic influences and pH conditions that are different for the release (pH ≈ 7.5) and sorption (pH ≈ 8.0) experiments (*24*).

Desorption distribution coefficients, K_d ($K_d = C_{solid}/C_{liquid}$), were estimated from the sequential extraction data. Here, C_{solid}, represents only the reversible sorbed fraction (defined as the sum of U(VI) in the extraction-based exchangeable, carbonate-associated, organic carbon bound and amorphous phases), and C_{liquid} indicates the U(VI) concentration in the aqueous phase. For comparison, K_d for the ORB was also obtained from previous sorption experiments (*24*). The results are shown in Table 2. Under the same pH conditions, desorption K_d from the extraction data are greater than K_d values from sorption experiments.

The release of U(VI) discussed here represents a transfer of an ion from the solid and adsorbed phases to the aqueous solution. The mechanisms responsible for U(VI) release include ionic exchange, dissolution, and complexation. Thus, differentiating solubilization from desorption is not possible using only macroscopic methods.

distinguishing desorption and solubilization of U(VI) requires spectroscopic information as well we bulk chemical analyses (*32*, *43*).

Summary

This research demonstrated that both ionic strength and V/M ratio influence the release of U(VI) from contaminated soil. Increasing the V/M ratio appears to be potentially much more efficient in promoting removal of U(VI) from soils than adjusting ionic strength with weak ligands such as NO_3^-. Release rates of U(VI) generally show an ionic strength and V/M ratio dependence, and an early fast release that gradually becomes slow over time. However, the dominant mechanisms responsible for U(VI) release (e.g., ionic exchange, desorption, solubilization, and complexation) are not clear. Calculated schoepite solubility under conditions relevant to the experiments is in the same range as the maximum U(VI) released from the calcareous contaminated soil, suggesting U(VI)-bearing mineral solubility may control U(VI) release from these soils.

We can also conclude that determining U(VI) fractions in soil through sequential extraction analysis is useful because it can enable evaluation of possible chemical methods for decontaminating soils. When mineral- structured U(VI) is dominant in a soil's uranium inventory, inefficient chemical removal can be anticipated.

Acknowledgments

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Table Captions:

Table 1. Characterization of the soils used in the experiments.

Table 2. Comparison of desorption and sorption K_d of U(VI) for two soils considered.

Figure Captions:

Figure 1.   U(VI) released from the FRC area 2 soil as a function of Ionic Strength
a. U(VI) concentrations released versus ionic strength; b. log R_d versus Ionic Strength
Dashed lines are the fitting trend lines. Solid line indicates U(VI) solubility as a function of ionic strength at pH 7.5.

Figure 2.   U(VI) chemical forms in the OR2, ORB, and AP soils used in this study
a. U(VI) concentration ($\mu g\ g^{-1}$) versus U(VI) forms; b. Percentage versus U(VI) forms.

OR2 : FRC Area 2 soil; AP: Altamont soil; ORB: FRC background soil
WS: Water soluble U(VI); EX: Exchangeable U(VI); CA: Carbonate associated U(VI); OA: Organic carbon bound U(VI); AA: Amorphous phases related U(VI); MA: Mineral associated U(VI).

Figure 3. U released normalized to the total extractable U(VI) in the OR2 soil as a function of ionic strength.
Dashed lines are the fitting trend lines. Solid line stands for removal ratios of U(VI) estimated from schoepite solubility and the total extractable U(VI) in the OR2 soil.

Figure 4.   Logarithmic release rates of U(VI) as a function of time at different ionic strengths.
Dashed lines are the fitting trend lines.

Figure 5.   Calculated schoepite solubility as a function of ionic strength within a pH range of 7.3 to 7.7.
Dashed lines are the fitting trend lines

Figure 6.   U(VI) released from the OR2 soil as a function of V/M ratio
a.U(VI) concentration released versus V/M ratio; b. log R_d versus as V/M ratio
Dashed lines are fitting trend lines. Solid line denotes schoepite solubility as a function of V/M ratio at pH 7.5.

Figure 7.   U released normalized to the total extractable U(VI) in the OR2 soil as a function of V/M ratio .
Dashed lines are fitting trend lines. Solid line represents removal ratios of U(VI) estimated from calculated schoepite solubility and the total extractable U(VI) in the OR2 soil.
Dashed lines are the fitting trend lines

Figure 8.   Logarithmic release rates of U(VI) as a function of time at different V/M ratios.
Dashed lines are the fitting trend lines

Figure 9.   Calculated schoepite solubility as a function of V/M ratio within a pH range of 7.3 to 7.7.
Dashed lines are the fitting trend lines

Figure 10.   Correlation of R_d from V/M dependent batches and K_d from sorption experiments versus U(VI) concentrations.
OR2-R denotes day 4 release results from the present study.

Table 1.

	ORB soil	OR2 soil	AP soil
Sand (%)	44.5	30	10.0
Silt (%)	43.0	41	61.7
Clay (%)	12.5	29	28.3
Calcite (%)	0.1	3.0	10.0
Extractable iron (mg g^{-1}) [b]	3.65		2.36
Total U (µg g^{-1}) (Acid Digested) [a]	0.89	206	
Extractable U(VI) [b]	0.70	102	
Water-extractable Organic Carbon (µg g^{-1})[a]	7.72	14.43	0.2

Water-extractable Native Inorganic Carbon ($\mu g\ g^{-1}$)[a]	14.43	73.6	

a. Data are from Pena et al.(23); b.This study.

Table 2

Sample No.	$\log K_d$ ($mL\ g^{-1}$)	$\log K_d$(sor) ($mL\ g^{-1}$)
ORB	3.66±0.05	3.25±0.04
AP	3.07±0.08	2.86±0.05
OR2	2.96±0.04	

Notes: In K_d, Csolid reflects the sum of U(VI) in exchangeable,
organic carbon bound, carbonate associated, and amorphous phases.
$K_{d\ sor}$ indicate K_d values from sorption experiments.
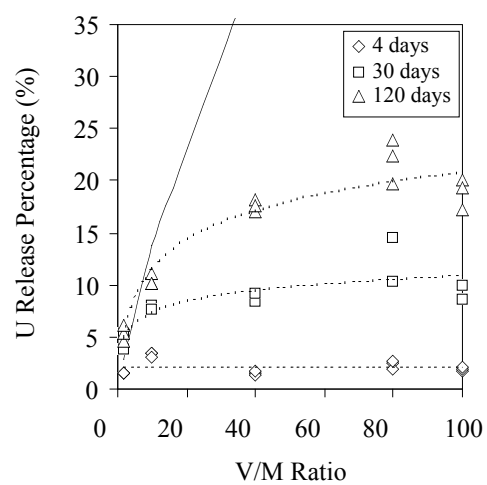
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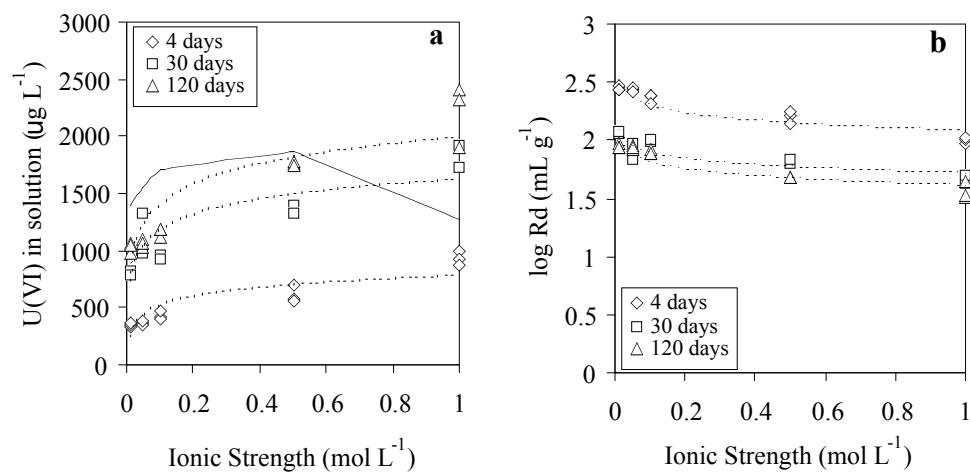
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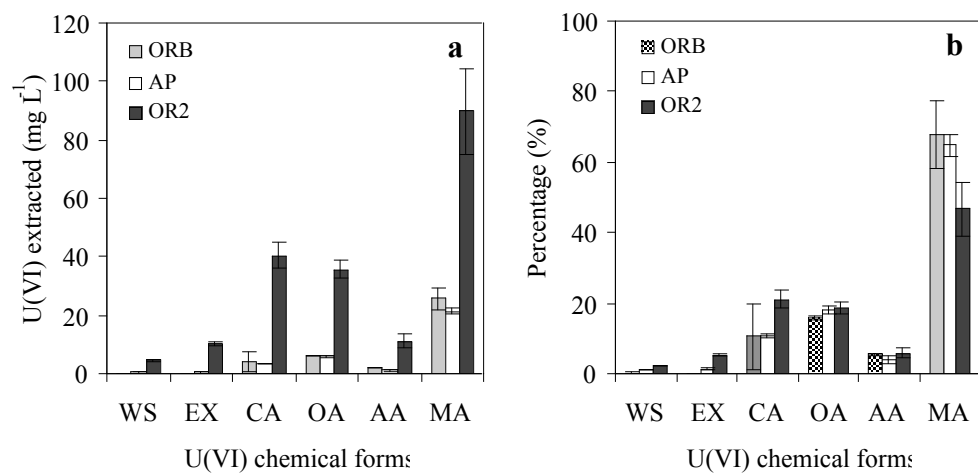
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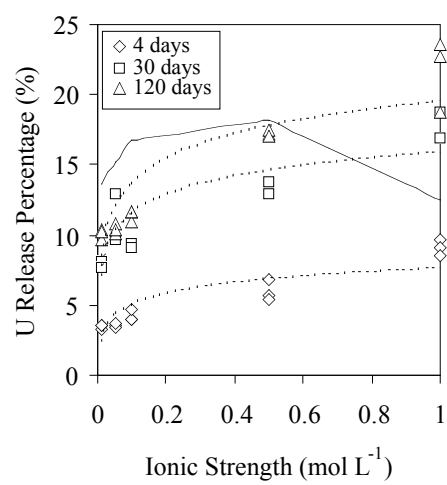
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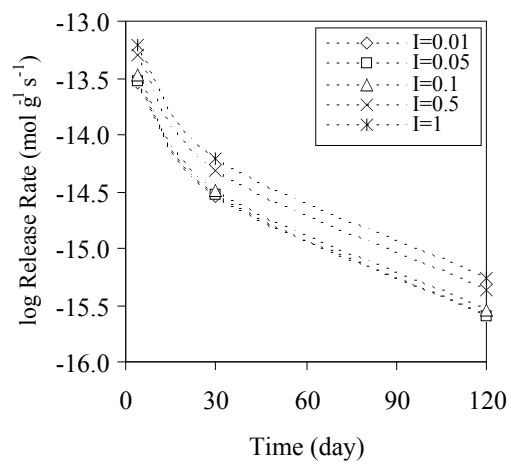
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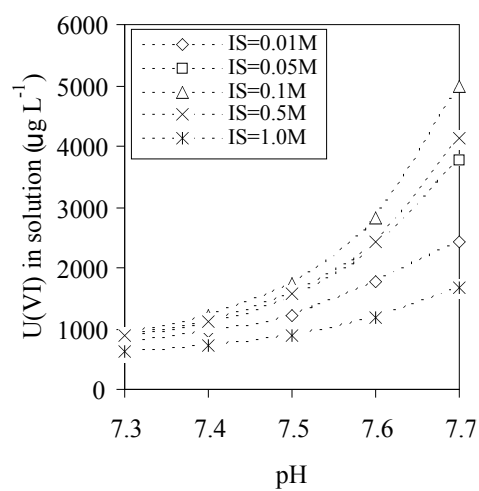
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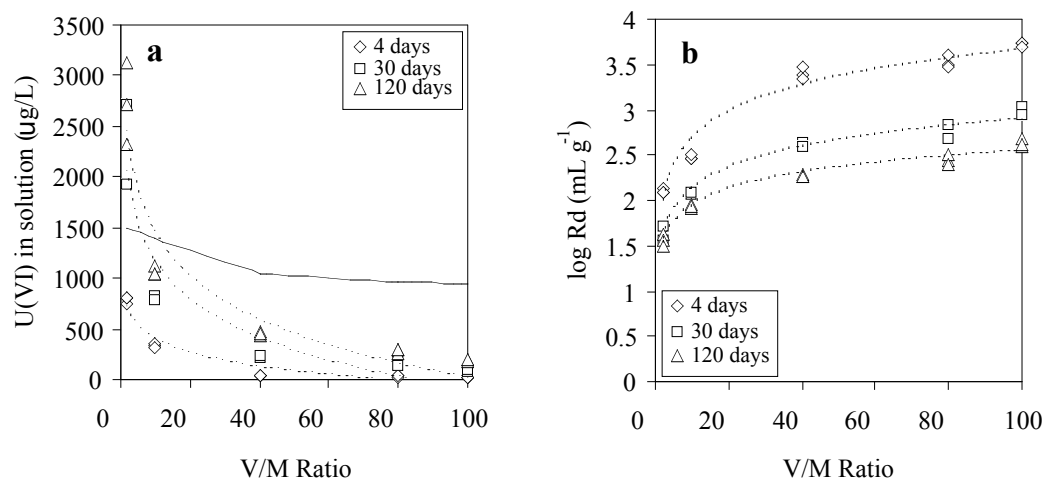
Figure 7

Figure 8

Figure 9

Figure 10